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1:30 PM-5:00 PM Javits Convention Center -- 1A15/1A16

***Environmental Management Science Program on Nuclear Waste Management***  
**Separations Chemistry and Technology**

Presiding: Roland Hirsch

Organizer: Tiffany Zachry

- 1:30 PM      Introductory Remarks
- 1:40 PM    85    Novel fission-product separation based on room -temperature ionic liquids  
             **Huimin Luo**, Sheng Dai
- 2:00 PM    86    Supercritical fluid extraction of radionuclides - A green technology for nuclear waste management  
             **Chien M. Wai**
- 2:20 PM    87    Fundamental chemistry of the universal extractant (UNEX) for the simultaneous separation of  
             major radionuclides (cesium, strontium, actinides, and lanthanides) from radioactive wastes  
             R. Scott Herbst, Dean R. Peterman, **Thomas A. Luther**, Vasily A. Babain, Igor V. Smirnov, Evgenii  
             S. Stoyanov
- 2:40 PM    88    Next generation extractants for cesium separation from High-Level Waste: From fundamental  
             concepts to site implementation  
             **Peter V. Bonnesen**, Nancy L. Engle, Maryna G. Gorbunova, Tamara J. Haverlock, Bruce A.  
             Tomkins, Eve Bazelaire, Lætitia H. Delmau, Bruce A. Moyer
- 3:00 PM      Intermission
- 3:25 PM    89    Supramolecular chemistry of environmentally relevant anions  
             **Kristin Bowman-James**, B.A. Moyer, Joanthan L. Sessler
- 3:45 PM    90    Exploiting ultra tight-binding ligands for separations technologies  
             Daryle Busch, **Richard S. Givens**, Xiaobin Zuo, Chi Zhang, Donnati Mosha, Jong-III Lee, K. Mani  
             Bushan, Mansour M. Hassan, Galen Loving
- 4:05 PM    91    Organofunctional sol-gel materials for toxic metal separation  
             Hee-Jung Im, Terry L. Yost, Yihui Yang, J. Morris Bramlett, Xiang-Hua Yu, Bryan C. Fagan,  
             Leonardo R. Allain, Tianniu Chen, **Ziling Xue**, Craig E. Barnes, Sheng Dai, Lee E. Rocker, Michael  
             J. Sepaniak
- 4:25 PM    92    Application of ionic liquid technologies to nuclear separations  
             **Robin D. Rogers**, John D Holbrey, Scott K. Spear, Keith E. Gutowski, Nicholas J. Bridges, Violina  
             A. Cocalia, Richard P. Swatloski
- 4:45 PM      Concluding Remarks

***Environmental Management Science Program on Nuclear Waste Management***  
**Separations Chemistry and Technology**

**ABSTRACTS**

**NUCL 85 [657025]: Novel fission-product separation based on room-temperature ionic liquids**

**Huimin Luo**, Nuclear Sciences & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, [luoh@ornl.gov](mailto:luoh@ornl.gov), and Sheng Dai, Chemical Sciences Division, Oak Ridge National Laboratory

**Abstract**

A new solvent extraction process for separation of cesium-137 and strontium-90 from high-level wastes based on room-temperature ionic liquids has been studied. Room-temperature ionic liquids that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species. A very unique intrinsic property of these melts is that they consist only of ions and that they can be made hydrophobic. The dual properties of these new ionic liquids make them efficient solvents for the extraction of ionic species from aqueous solutions. In this presentation, we will discuss our recent results on the solvent extraction of Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> by ionic liquids containing calix[4]arene-bis(tert-octylbenzo-crown-6)(BoBcalixC6) and dicyclohexano-18-crown-6 (DCH18C6). We will also present the synthesis of several new DCH18C6 derivatives with one of the oxygen atoms replaced by an azo group. With these new crown ethers, we are able to recycle crown ethers after the extraction experiments for metal cations in ionic liquids by pH modulation.

**NUCL 86 [657301]: Supercritical fluid extraction of radionuclides - A green technology for nuclear waste management**

**Chien M. Wai**, Department of Chemistry, University of Idaho, Renfrew Hall, Moscow, ID 83844, Fax: 208-885-6173, [cwai@uidaho.edu](mailto:cwai@uidaho.edu)

**Abstract**

Supercritical fluid carbon dioxide (SF-CO<sub>2</sub>) is capable of extracting radionuclides including cesium, strontium, uranium, plutonium and lanthanides directly from liquid and solid samples with proper complexing agents. Of particular interest is the ability of SF-CO<sub>2</sub> to dissolve uranium dioxide directly using a CO<sub>2</sub>-soluble tri-n-butylphosphate-nitric acid (TBP-HNO<sub>3</sub>) extractant to form a highly soluble UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> complex that can be transported and separated from Cs, Sr, and other transition metals. This method can also dissolve plutonium dioxide in SF-CO<sub>2</sub>. The SF-CO<sub>2</sub> extraction technology offers several advantages over conventional solvent-based methods including ability to extract radionuclides directly from solids, easy separation of solutes from CO<sub>2</sub>, and minimization of liquid waste generation. Potential applications of the SF-CO<sub>2</sub> extraction technology for nuclear waste treatment and for reprocessing of spent nuclear fuels will be discussed. Information on current demonstrations of the SF-CO<sub>2</sub> technology by nuclear companies and research organizations in different countries will be reviewed.

**NUCL 87 [656556]: Fundamental chemistry of the universal extractant (UNEX) for the simultaneous separation of major radionuclides (cesium, strontium, actinides, and lanthanides) from radioactive wastes**

**R. Scott Herbst**<sup>1</sup>, Dean R. Peterman<sup>1</sup>, Thomas A. Luther<sup>1</sup>, Vasily A. Babain<sup>2</sup>, Igor V. Smirnov<sup>2</sup>, and Evgenii S. Stoyanov<sup>3</sup>. (1) INEEL, 1625 N. Fremont Avenue, PO Box 1625, Idaho Falls, ID 83415-2208, Fax: 208-526-8541, herbrs@inel.gov, (2) Khlopin Radium Institute, (3) Institute of Catalysis

**Abstract**

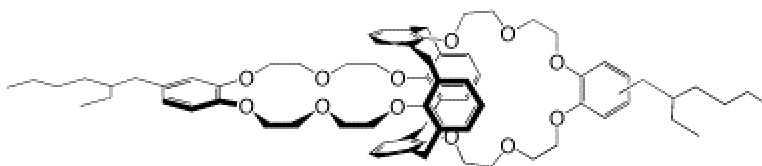
Scientists at the INEEL and KRI collaboratively developed and validated the concept of a Universal Extractant (UNEX) for simultaneously removing the major radionuclides (Cs, Sr, actinides, and lanthanides) from acidic radioactive waste in a single solvent extraction process. The UNEX solvent incorporates three active extractants: chlorinated cobalt dicarbollide, polyethylene glycol, and a carbamoylmethylphosphine oxide derivative, dissolved in a suitable organic diluent to simultaneously extract target radionuclides. The process chemistry is unique, but complicated, since the extractants operate synergistically to extract the radionuclides. Furthermore, interactions with the diluent are quite important as the diluent strongly influences the extraction properties of the solvent system. We are currently studying the fundamental chemical phenomena responsible for the selective extraction of the different species to understand the underlying mechanisms and facilitate enhancements in process chemistry. Our efforts to date have relied on a combination of classical chemistry techniques, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to identify and explain the structures formed in the organic phase, elucidate the operative chemical mechanisms, and evaluate the diluent effects on extraction properties.

**NUCL 88 [642053]: Next generation extractants for cesium separation from High-Level Waste: From fundamental concepts to site implementation**

**Peter V. Bonnesen**, Nancy L. Engle, Maryna G. Gorbunova, Tamara J. Haverlock, Bruce A. Tomkins, Eve Bazelaire, Lætitia H. Delmau, and Bruce A. Moyer, Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6119, Oak Ridge, TN 37831-6119, Fax: 865-574-4939, bonnesenpv@ornl.gov

**Abstract**

The successful development of the Caustic-Side Solvent Extraction (CSSX) process at ORNL owes a great deal to basic scientific concepts uncovered and discoveries made through research programs funded both by the US DOE's Basic Energy Sciences and Environmental Management Science Programs. Under the EMSP, we have been designing, synthesizing and characterizing new calixarene-crown ethers for cesium extraction. Scientific issues we are addressing with the new extractants include increasing hydrocarbon solubility, and improving the efficiency of cesium ion binding and release. The fundamental chemistry and extraction behavior of these new calixarene crowns will be discussed.



**NUCL 89 [655952]: Supramolecular chemistry of environmentally relevant anions**

**Kristin Bowman-James**, Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045, Fax: 785-864-5396, kbowman-james@ku.edu, B.A. Moyer, Oak Ridge National Laboratory, and Joanthan L. Sessler, Department of Chemistry and Biochemistry, The University of Texas at Austin

**Abstract**

The goal of this project is the development of highly selective extractants for anions targeting important and timely problems of critical interest to the EMSP mission. In particular, sulfate poses a special problem in cleaning up the Hanford waste tanks in that it interferes with vitrification, but available technologies for sulfate removal are limited. The basic chemical aspects of anion receptor design of functional pH independent systems as well as design of separations strategies for selective and efficient removal of targeted anions have been probed. Key findings include: (1) some of the first synthetic sulfate-selective anion-binding agents; (2) simple, structure-based methods for modifying the intrinsic anion selectivity of a given class of anion receptors; and (3) the first system capable of extracting sulfate from acidic, nitrate-containing aqueous media. Receptor design, structural influences on anion binding affinities, and findings from liquid-liquid extraction studies will be discussed.

**NUCL 90 [656120]: Exploiting ultra tight-binding ligands for separations technologies**

Daryle Busch, **Richard S. Givens**, Xiaobin Zuo, Chi Zhang, Donnati Mosha, Jong-Ill Lee, K. Mani Bushan, Mansour M. Hassan, and Galen Loving, Department of Chemistry, University of Kansas, 1251 Wescoe Hall Dr, Malott Hall, Lawrence, KS 66045, Fax: 785-864-5296, dbusch@eureka.chem.ukans.edu

**Abstract**

The classic slowness that has kept the most powerful ligands from being used in separations applications is under attack in two ways: (1) replacing metal ion - ligand equilibration with switch binding and release as the mode of complexation. By exploiting the tight-binding capabilities of cryptands, the capture of selected metal ions isolates them from their environment. These cryptands are constructed with photoactivatable functions that sever the cryptand, releasing encapsulated metal ions. The precursors have been modified to capture the metal ion concomitant with cryptate formation. (2) developing a methodology (the soil poultice) so slow that powerful ligands can be used. A solution containing the specially designed ligand is mixed with a solid macroporous imprinted polymer (MIPs) and applied to the contaminated area. The ligand captures the metal ion and the MIPs captures the resulting complex. Current studies focus on combinations of MIPs-complex interactions to optimize strength of binding and selectivity.

**NUCL 91 [655519]: Organofunctional sol-gel materials for toxic metal separation**

Hee-Jung Im<sup>1</sup>, Terry L. Yost<sup>1</sup>, Yihui Yang<sup>1</sup>, J. Morris Bramlett<sup>1</sup>, Xiang-Hua Yu<sup>1</sup>, Bryan C. Fagan<sup>1</sup>, Leonardo R. Allain<sup>1</sup>, Tianniu Chen<sup>1</sup>, **Ziling Xue**<sup>1</sup>, Craig E. Barnes<sup>1</sup>, Sheng Dai<sup>2</sup>, Lee E. Rocker<sup>3</sup>, and Michael J. Sepaniak<sup>1</sup>. (1) Department of Chemistry, The University of Tennessee, Knoxville, TN 37996, Fax: 865-974-3454, xue@utk.edu, (2) Chemical Sciences Division, Oak Ridge National Laboratory, (3) Department of Chemistry, Berea College

**Abstract**

Inorganic-organic silica sol-gels grafted or encapsulated with organic ligands were prepared and found to selectively and reversibly remove target metal ions such as Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Sr<sup>2+</sup>. These organofunctional sol-gel materials, which were easily prepared from off-the-shelf chemicals, were hydrophilic and showed fast kinetics of metal uptake. The sol-gels were easily regenerated and used in multi-cycle metal removal. In our search for new ligands for metal removal, we found that the reactions of thioacetal ligands with Hg<sup>2+</sup> gave Hg(SCH<sub>2</sub>COOH)<sub>2</sub>. Our studies of organofunctional sol-gel materials for metal separation will be discussed.

**NUCL 92 [655353]: Application of ionic liquid technologies to nuclear separations**

**Robin D. Rogers**, John D Holbrey, Scott K. Spear, Keith E. Gutowski, Nicholas J. Bridges, Violina A. Cocalia, and Richard P. Swatloski, Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, AL 35487, RDRogers@bama.ua.edu

**Abstract**

Room temperature Ionic Liquids (ILs), organic salts that are liquid at, or close to room temperature have great potential application for uses in liquid-liquid separations processes. As a class of liquids, ILs typically have wide liquid ranges, are non-volatile, and have solvent characteristics (hydro- and lipophilicity, hydrogen-bond donor and acceptor ability etc) that can be controlled and modified by suitable changes to either the cation or anionic components of the IL. We have begun the exploration of actinide separations using a variety of technologies based upon the use of ILs including, liquid/liquid extraction using traditional extractants; incorporating an extractant functionality into an IL; immobilizing IL extractant phases on solid supports; and utilization of the solubilizing power of ILs to prepare cellulose-based materials for f-element separations. ILs can thus be considered as a new class of materials for nuclear separations, distinct from molecular solvents and from high temperature molten salts, with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of “green” chemistry in various chemical processes.